

Magneto-Ionics: magnetic switching via ion intercalation in solid-state battery structures

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The current digital information age is characterized by a growing need for efficient devices for data storage and computation. Magnetic devices have long been used for data storage, as evidenced by the use of magnetic tapes and hard disk drives in early computers. However, data storage for worldwide internet search engines is currently dominated by semiconductor-based memory devices, specifically in the form of dynamic random-access memory (DRAM) cells,¹ which were invented in the 1960s by Robert Dennard at IBM.² Each DRAM cell consists of a capacitor and a transistor: information is stored based on the amount of charge that is stored in the capacitor, and that information is communicated to the rest of the device through the transistor. Although DRAMs are advantageous for their high speed and low cost, it is a volatile form of memory – the information is stored only as long as electricity flows through the device. The late 1980s and early 1990s saw the discovery of the giant magnetoresistance (GMR) effect and tunneling magnetoresistance, which more recently have been used to develop non-volatile magnetic random-access memory (MRAM) devices.¹

The GMR effect is seen in alternating nanometer-scale thin films of ferromagnetic metals and nonmagnetic metals. The magnetization of each of the ferromagnetic layers can be aligned in either a parallel or antiparallel configuration, which corresponds to a low resistance and high resistance state, respectively (Figure 1).

A similar concept is utilized in magnetic tunnel junctions (MTJs) which make use of tunneling magnetoresistance. An MTJ consists of two ferromagnetic electrode layers separated by a thin, nonmagnetic, insulating spacer material. Electrons can tunnel between the electrodes when the magnetization directions of the electrodes are parallel, whereas no tunneling occurs for an antiparallel magnetization. Overall, switching the magnetization direction of ferromagnetic materials (in response to an applied magnetic field) in a device will change the resistance of the device. The ferromagnetic nature of the materials ensures that this switch in magnetization is maintained after the applied magnetic field is turned off. This phenomenon allows information to

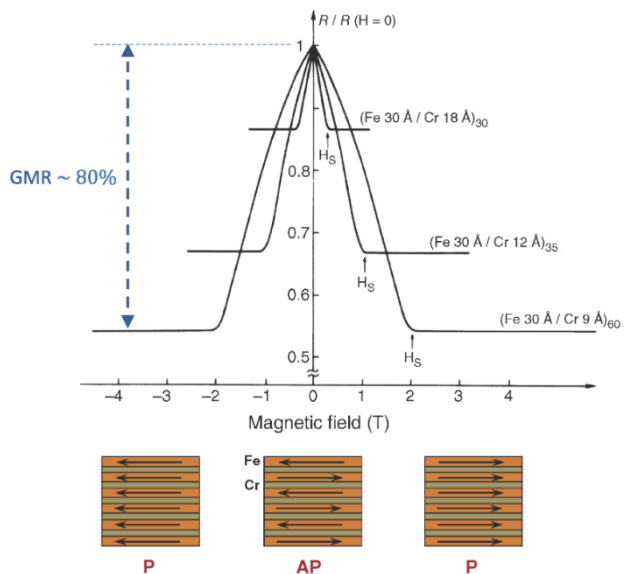


Figure 1. Normalized resistance as a function of external magnetic field for Fe/Cr multilayers. Taken from reference 1.

be stored in the form of a magnetic state, which can be communicated through integrated electronic circuits without the need for sustained current flow in the memory device itself.

The use of magnetoresistance in memory devices established the field of spintronics. Spintronics exploits the spin properties of electrons in materials to manipulate the magnetism displayed by those materials. Whereas conventional electronic devices focus only on the flow of charge, spintronics also consider the spin state of charge carriers. In addition to non-volatility, memory devices based on spintronics have low energy dissipation, high endurance, and scalability advantages over memory devices based on conventional semiconductor electronics such as complementary metal-oxide semiconductor (CMOS) technology and dynamic random access memory (DRAM) devices.¹ Outside of memory, spintronics has allowed magnetic devices to be used for computation based on machine learning. For example, MTJs that switch based on current via spin transfer torque are being developed as ‘neurons’ in neuromorphic computing systems for machine learning as well as spin-transfer torque random access memory (STT-MRAM).

Recent efforts to optimize spintronic devices include the exploration of voltage or electric field control of magnetism as an alternative to magnetic field control. This approach provides an opportunity to create low power spintronic devices that experience large changes in magnetization direction or saturation magnetization in response to small changes in applied voltage, further reducing the amount of energy that is required for magnetic data storage and memory. One method to achieve voltage-controlled magnetism involves the accumulation of charges at surfaces and interfaces.³ However, this electrostatic approach to magnetic switching is a volatile form of magnetic control that is limited to the magnetic interface, neglecting the bulk of the material.

A non-volatile approach to voltage-controlled magnetism is found in magneto-ionics. The field of magneto-ionics uses the conduction of ions in response to an applied electric field to alter the composition of a material, which in turn alters the magnetization of the material. The movement of ions is relatively slow, but the non-volatile voltage-control of magnetism is ideal for spintronic devices.⁴

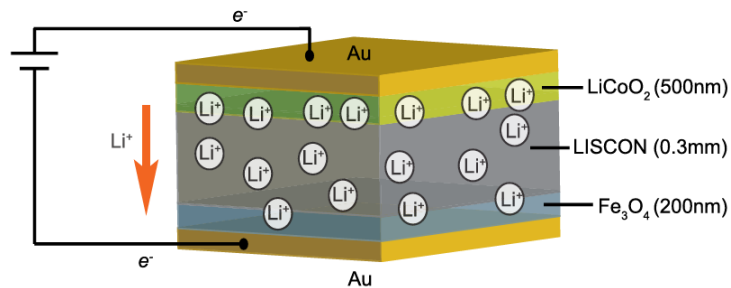


Figure 2. Schematic of all solid state film battery used to study the effect of lithium ion intercalation on magnetic properties of Fe_3O_4 films. Taken from reference 5.

Although magneto-ionics based on the motion of ions in oxygen conductors and proton conductors has been studied, a newer direction of the field investigates the intercalation of lithium ions as seen in solid-state battery structures (Figure 2).⁴ A solid state-battery consists of an ion conducting solid electrolyte sandwiched between electrode materials. In magneto-ionic studies, the electrodes are magnetic materials whose properties change with changes in mobile-ion content. The electrolyte facilitates ionic movement in response to a voltage applied across the electrodes. This property makes solid-state battery structures ideal testbeds for investigating magnetic changes

in response to voltage-induced ionic motion. The properties of lithium ions that make them ideal for batteries – small size, fast diffusion kinetics, and reversible intercalation – also make them ideal for studies of magneto-ionic phenomena.

Reversible electric-field control of magnetoresistance of Fe_3O_4 via lithium ion intercalation in a solid state battery structure was demonstrated in 2016 by Tsuchiya et al.⁵ About a year later, Wei et. al. used an all-solid-state lithium ion battery structure to demonstrate the reversible effect of lithium ion intercalation on the saturation magnetization of a spinel Fe_3O_4 anode material⁶. However, existing spintronic devices can change the direction of magnetization in a material without altering its saturation magnetism. This change in both direction and saturation seen by Tsuchiya and Wei is common for magnetic switching achieved via ion intercalation. To address this, Ameziane et al. fabricated a solid-state lithium ion battery structure to switch the magnetization direction of a Co/Pt layered anode material via lithium ion intercalation without altering its saturation magnetization (Figure 3).⁴

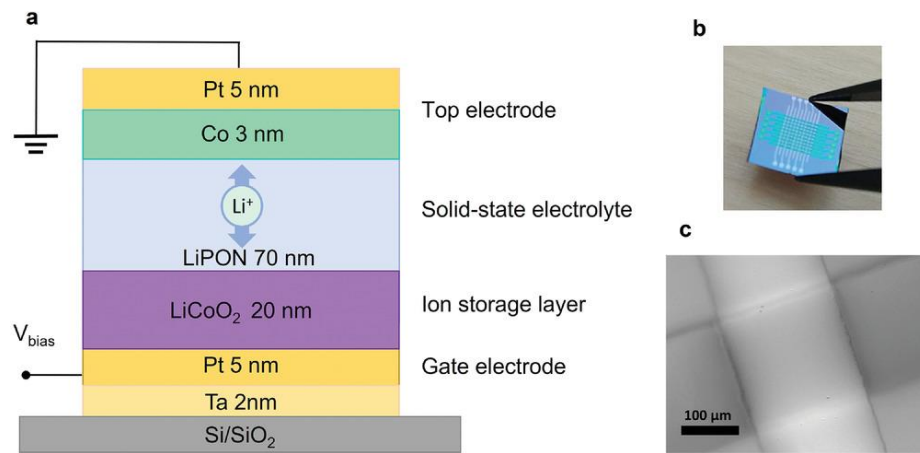


Figure 3. a) Magneto-ionic solid state battery structure. b) Image of a $10 \times 10\text{mm}^2$ sample with crossbar junctions. c) Close-up of the patterned battery structure. Taken from reference 4.

The interlayer Ruderman–Kittel–Kasuya–Yosida (RKKY) coupling can also be modulated by magneto-ionic effects. Ameziane et al. built up the Co/Pt anode to have a nonmagnetic Ru layer sandwiched between two ferromagnetic Co/Pt multilayers. This coupling originates from spin-dependent reflections of electron wavefunctions at the magnetic-nonmagnetic interface, which cause the sample to oscillate between ferromagnetic (FM) and antiferromagnetic (AFM) states as a function of the Ru thickness. Not only is the strength of the coupling modulated under an applied voltage, but the phase changes as well near FM-AFM inflection points.⁸

Overall, magneto-ionic devices based on lithium ion battery stacks are promising candidates for non-volatile magnetic switching in a variety of applications. As the investigation of magneto-ionic effects in solid state battery structures expands, new approaches in research and development will be essential to facilitate the implementation of such devices. First, it is necessary to explore alternatives to lithium and cobalt containing materials to avoid intensifying the already strained demand for such materials for renewable energy applications. Additionally, as MTJs have shown compatibility with CMOS technology, this ion-driven magnetic switching must be tested for implementation with CMOS technology, integrated circuits, and larger magnetic memory systems to ensure their operation is stable under realistic operation conditions. Further, the

fabrication of such thin film samples must be made more practical and scalable if these devices are to replace DRAM in the data storage market.

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